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Second-Order Møller−Plesset Perturbation Theory for Systems Involving First Transition Row Metals

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Results obtained using second-order Møller−Plesset (MP2) perturbation theory are compared with those obtained using coupled cluster singles and doubles approach including a perturbational estimate of the connected triple excitations, CCSD(T), or the modified coupled-pair functional (MCPF) approach. For FeCO, $FeCO^+$, FeH_2O^+, and the states of $FeCH_4^+$ derived from the Fe^+ $3d^64s^1$ occupation, the MP2 geometries are found to be in good agreement with those obtained at the CCSD(T) or MCPF level. At the MP2 level the Fe−C bond lengths for the states of $FeCH_4^+$ derived from the $3d^7$ occupation are too long relative to the MCPF or CCSD(T) results. The geometries computed at the self-consistent-field (SCF) level are quite poor for $FeCO^+$ and all states of $FeCH_4^+$. The energetics at the MP2 level, while superior to the SCF, are still significantly inferior to those obtained at the CCSD(T) or MCPF level. We find that $FeCH_4^+$ has a quartet ground state with an η^3 coordination.

I. Introduction

The number and quality of calculations involving transition metals have increased dramatically in the past few years.[1] It has been found that it is even more important to include extensive correlation to obtain accurate energetics for transition metal systems than for nonmetal systems. Geometries determined at the self-consistent field (SCF) level have been found to be reasonably accurate for many covalently bonded systems.[2,3] For electrostatically bonded systems with some dative bonding, the SCF can underestimate the dative bonding and lead to metal−ligand bond lengths that are too long.[4] In addition to these problems with the geometry, the SCF overestimates the frequencies of intraligand modes but underestimates them for the metal−ligand modes.[4] Thus, there is no simple scaling which can improve the frequencies (and hence the calculation of the zero-point energy). To avoid these limitations of the SCF geometry, in many of our previous studies[1] of the first and second transition row systems we optimized the geometry at the modified coupled-pair functional[5] (MCPF) level. That is, the geometry was optimized at the same level of theory that was used to determine the accurate energetics. While this works well for small systems, it can clearly become prohibitively expensive for large systems. In these cases we partially optimized the geometries at the MCPF level, with the remaining parameters taken from the optimal SCF geometry. While this works reasonably well, it is still time-consuming and somewhat arbitrary in the choice of which parameters are optimized. In addition, the MCPF approach is not suitable for the calculation of vibrational frequencies except for small systems, because analytic derivatives have not been implemented.

It should be noted that these problems associated with the SCF approach appear to be much more severe for the first transition row. In fact, Siegbahn and co-workers[3] have found *that the SCF geometries are* reasonably accurate for molecules containing second transition row atoms, with only a few cases where the SCF fails. They routinely optimize the geometry at the SCF level and only compute the energetics using a correlated approach in a large basis set.

With this work of Siegbahn and co-workers[3] in mind, we used[4] second-order Møller−Plesset perturbation theory[6] (MP2) to optimize the geometry and compute the frequencies of several VL^+, CoL^+, and CuL^+ systems. The results showed that MP2 performed reasonably well for the geometry and frequencies but that higher levels of correlation were required to compute accurate binding energies. While the MP2 approach is more expensive than the SCF, it is still practical to optimize the geometry and compute the frequencies at this level, because analytic second derivatives have been developed[7] for the MP2.

In this work we extend our tests to include systems with Fe, because the Fe atom population in FeL and FeL^+ can be between six and seven 3d electrons and correlation is known to be important in correctly establishing the correct mixing of these two limits. We consider FeCO and $FeCO^+$. Both are known[8,9] to bond from the Fe excited state with a $3d^7$ occupation because this maximizes Fe to CO $2\pi^*$ donation, which is much larger for FeCO than for $FeCO^+$. We study FeH_2O^+, which is known[10] to bond from the $3d^64s^1$ Fe^+ ground state. There is very little dative bonding in this case. We also study $FeCH_4^+$, where the bonding mechanism is expected to involve CH_4 to metal donation.[4,11] The MCPF calculations of Perry and Goddard[12] predict a quartet state, while Schultz and Armentrout[13] predict a sextet state. However, this latter prediction is based only on the trends in the experimental successive binding energies for $Fe(CH_4)_4^+$.

II. Methods

The geometries are optimized using a small basis set, and final binding energies are computed using the MCPF approach in a large basis set. The large Fe basis set is the (20s12p9d6f4g)/[(6 + 1)s(5 + 1)p4d2f1g] described previously,[14] with a set of g polarization functions included. The remaining large basis sets are the augmented correlation consistent polarized valence triple-zeta sets of Dunning and co-workers.[15] The small Fe set is a [8s4p3d] contraction of the (14s9p5d) primitive set developed by Wachters.[16] The s and p spaces are contracted using contraction number 3, while the d space is contracted (311). To this basis set are added two diffuse p functions; these are the functions optimized by Wachters multiplied by 1.5. A diffuse d function[17] and an f polarization ($\alpha = 1.339$) are added.

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